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ELECTRODE KINETICS OF THE ALKALI METALS IN $AlCl_3$ PROPYLENE CARBONATE SOLUTION

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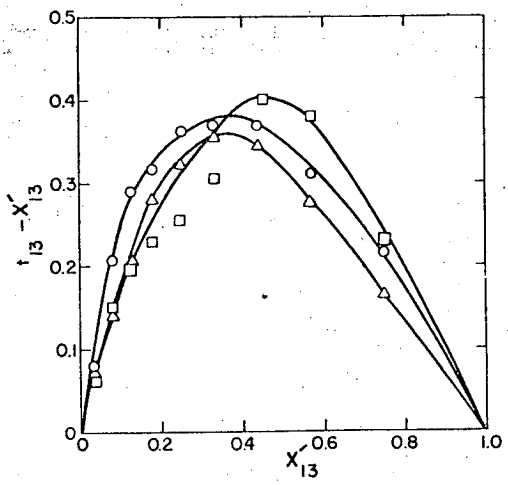

Fig. 4. (t_{13} — x'_{13}) vs. x'_{13} plots for the systems LiCl-$CeCl_3$ (○), NaCl-$CeCl_3$ (△), and KCl-$CeCl_3$ (□).

show that the alkali ions possessed relatively larger mobility than the cerous ion over the whole composition range of the mixtures.

Acknowledgment

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Electrode Kinetics of the Alkali Metals in $AlCl_3$-Propylene Carbonate Solution

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ABSTRACT

Kinetic parameters of the deposition-dissolution process for solid alkali metals in alkali metal chloride-$AlCl_3$-propylene carbonate solution were evaluated using micropolarization measurements at 25°C. The exchange current densities were evaluated at different molalities of the alkali metal chlorides, and the cathodic transfer coefficients were calculated from the concentration dependence.

Interest in nonaqueous high energy batteries is reflected in an increasing number of investigations concerning the electrochemical behavior of active metals in nonaqueous solvents. So far very few investigations have reached the stage of evaluating kinetic parameters of the charge transfer process. The feasibility of electrodeposition of all the alkali metals from the corresponding solutions of the alkali metal chlorides in $AlCl_3$-propylene carbonate has been demonstrated (1). Lithium, sodium, potassium, rubidium, and cesium were deposited at ambient temperature, showing stable and reversible behavior. The alkali metal chlorides are practically insoluble in PC, however in the presence of $AlCl_3$, a complex is formed between the chloride and $AlCl_3$ according to the reaction

$$MCl + AlCl_3 = M^+ + AlCl_4^- \quad [1]$$

where M represents the alkali metal. This reaction is responsible for high solubility and conductivity of all the alkali metal halides in PC; it allows the study of the electrochemical behavior of alkali metals with a common anion species.

In the present work, kinetic parameters of the deposition-dissolution process for solid alkali metals in alkali metal chloride-$AlCl_3$-PC solutions have been evaluated using micropolarization measurements at 25°C. The micropolarization experiments were conducted over a range of alkali metal chloride molalities (0.01-1.0*M*) in constant unit molality solutions of $AlCl_3$ in PC.

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Key words: electrode kinetics, alkali metals, propylene carbonate, exchange current density, transfer coefficient.

Previous Work

Despite the increasing interest in dissolution-deposition processes in nonaqueous solutions, few investigations dealt directly with the kinetics of the electrode process. Moreover, most of the literature dealt exclusively with lithium systems. Although the work of Harris and Tobias (2) included deposition tests of active metals from cyclic esters, these were mostly qualitative in nature and did not reach the stage of systematic kinetic measurements.

The electron transfer kinetics of Li/Li^+ reaction in PC was studied by several laboratories. Burrows and Jasinski (3) measured the exchange current density of Li(s) in 1M $LiClO_4$-PC at 28°C, using micropolarization measurements. However, the reported exchange current density appears too low (0.0275 mA/cm^2), probably due to the inclusion of an ohmic drop in the potential measurements. Meibuhr (4) measured the exchange currents of lithium in different $LiClO_4$ concentrations in PC, at temperatures up to 70°C. At 28°C, for 1M $LiClO_4$-PC solution, the exchange current, i_o = 0.95 mA/cm^2, and the transfer coefficient, α = 0.67, were calculated from the linear polarization curves and from the concentration dependence of the exchange current. The solution was stirred by bubbling argon, and the ohmic drop was excluded using a pulse technique. The Nernstian behavior of the lithium electrode was confirmed by concentration cells. The enthalpy of solvation at zero polarization was estimated as 8.5 kcal/mole, and the reaction order was one, which reaffirmed the assumption that the charge transfer was the rate-determining step. In a second article, Meibuhr (5) studied the anion effect on the electrode kinetics of Li/Li^+ in PC. The exchange currents for unit molarity solutions of $LiAlCl_4$, $LiPF_6$, and $LiBF_4$ are 0.40, 0.29, and 0.5 mA/cm^2, respectively. The transfer coefficient for $LiAlCl_4$ was α = 0.8. The water content of the solutions had a major influence on the electrode performance. Scarr (6) measured the kinetics of lithium electrode in different concentrations of $LiClO_4$ in PC. Film formation and two levels of activity were observed, depending on the pretreatment of the electrode. The film was broken at high currents. The exchange current density of a film-free electrode in 1M $LiClO_4$ PC solution is 1.78 ± 0.33 mA/cm^2. Generally, good agreement was found between Meibuhr's and Scarr's results, which are complementary, since Scarr worked at moderately high currents, while Meibuhr's work is restricted to the zone of linear current-potential dependence. Butler, Cogley, and Synnot (7) studied the aging effect on the kinetics of lithium in $LiClO_4$ solution in PC. Even when the solvent was quite "dry" (<0.001*M* H_2O), the exchange current dropped from 10.2 mA/cm^2 at 1 sec after the exposure of the freshly cut lithium surface, to 1.6 mA/cm^2 after 1 hr. The effect of water was also dramatic; the presence of 0.02*M* H_2O reduced the exchange current to 0.026 mA/cm^2 after 1 hr. It seems that most measurements were taken on aged surfaces; the exchange currents of fresh surfaces may have no practical meaning. The effect of water content on the behavior of lithium electrodes in $LiClO_4$ (8, 9) showed that LiOH was formed on the electrode during the deposition of lithium from $LiClO_4$ solution in PC.

The anodic polarization of lithium in 1.0*M* $AlCl_3$ PC solution was investigated by Jackson and Blomgren (10), using an interrupter and a constant load pulse technique. Severe polarization of the concentration type was observed, which could be caused by the formation of LiCl layer during the anodic discharge. Sufficient stirring removed the product which dissolved in $AlCl_3$ solution and eliminated the concentration polarization.

In a study of the anodic behavior of sodium in $NaClO_4$ PC solution, Meibuhr (11) reports that the exchange current depends strongly on the Na^+ concentration. At 1M $NaClO_4$ and at 19°C, the exchange current was 0.21 mA/cm^2.

The behavior of lithium in related solvents is reported in several papers. The electrochemical behavior of Li in solutions of $LiClO_4$, KPF_6, and of KCNS in ethylene carbonate was reported by Pistoia *et al.* (12, 13). Ethylene carbonate was proposed as a superior solvent for high energy batteries due to its higher conductance and lower viscosity, and due to the better anodic polarization characteristics found for Li in $LiClO_4$-EC solution.

The kinetics of Li(Hg) in LiCl solution in DMSO was reported by Cogley and Butler (14, 15). The Tafel equation with cathodic transfer coefficient α = 0.75 was obeyed over the current density range of 10^{-5} to 3×10^{-3} A/cm^2. The exchange currents were in the order of 0.1-1.0 mA/cm^2.

Tiedemann and Bennion (22) compared their kinetic measurements of Li in dimethyl sulfite to similar measurements in PC, however it should be kept in mind that their measurements were performed in different solvent, and medium effects must be considered as partly responsible for the higher exchange currents in dimethyl sulfite; the effect of the medium on the electrode kinetics is discussed in detail by Jorné (1).

Experimental

The micropolarization measurements of the alkali metals were performed in the same six-compartment cell where the cell potentials were measured (1, 16). The galvanostatic experiments were conducted between two alkali metal electrodes where the central one served as the working electrode. The central working electrode was prepared in the glove box by sealing an approximately 5 cm long portion of a bright alkali metal wire in epoxy resin. The end of the wire, not sealed in epoxy resin, was used for an electrical contact by attaching it to an alligator clip. The other end of the coated wire was cut at a right angle to the wire to expose the bright alkali metal surface with an area equal to the cross-sectional area of the wire. The other alkali metal electrodes were simply the original bright wires. Alkali metals react slowly with epoxy resin. The polarization experiments were performed within a few hours after the exposure and no signs of reaction between the metals and the resin were observed throughout the measurements. In addition, the small bias potentials between the coated and uncoated electrodes (1) indicate this effect to be negligible. In the case of rubidium and cesium, the working electrodes, as well as the counterelectrodes, were prepared by pouring the molten metals into the cup electrodes (1, 16). The solutions were stirred during the micropolarization experiments by a small magnetic stirrer at the bottom of the central cell, just under the electrode's surface. The stirring was somewhat less efficient in the cases of Rb and Cs because the stirrer was underneath the cup, while the active surface of the electrode was facing upward. The small currents employed insured that concentration overpotentials were negligible, even in the cases of Rb and Cs.

Preanodization was found necessary to obtain reproducible results. The standard procedure was to anodize the working electrode for 10 min at a current density of 0.1 mA/cm^2 prior to each micropolarization cycle. The potential was measured between the central working electrode and one of the two Tl(Hg)/TlCl reference electrodes. The current was increased first in the anodic direction, then back toward the cathodic direction, then back to the equilibrium state. The current was applied by a constant current power supply, Model C 612 Electronic Measurements, and was measured by a Keithley 601 Electrometer. The potential was measured by an AC/DC Differential Voltmeter (John Fluke Model 887-A). The cells were suspended in constant temperature baths at 25° and 35°C ± 0.01°C. The preparation of the electrodes and the assembly of the cells have been described previously (1, 16). Propylene carbonate (Jefferson Chemical Company, Hous-

ton, Texas) was distilled in a low pressure distillation column packed with stainless steel helices; the reflux ratio was 60 to 100; and the head temperature was 65°C. The solutions were treated with molecular sieves 4A. This treatment increased the stability of the alkali metals in the solutions. Gas chromatographic analysis showed the water content to be always below 50 ppm. All operations were conducted inside the argon glove box (1, 16). Addition of $AlCl_3$ to PC results in violent reaction, accompanied by high heat of solution and darkening of the solution. This was avoided by adding the alkali metal chloride first, then adding the $AlCl_3$ very slowly while cooling the solution with a cooling mixture of chloroform-carbon tetrachloride-dry CO_2 (1). Solutions prepared in this way were almost colorless. The stability of the solutions increased as the ratio of the alkali metal chloride to $AlCl_3$ molalities approached unity.

Because of the relatively low conductivity of the solutions (10^{-3}-10^{-2} ohm^{-1}-cm^{-1}), it was necessary to correct the overpotentials for ohmic drop between the working electrode and the tip of the reference electrode's connection. The ohmic drop was determined by a rapid current interrupter technique, in which the constant current was interrupted, and the potential was traced on a fast oscilloscope. The immediate drop in the potential was the *IR* drop, and the ohmic resistance was calculated by dividing it by the total current. The ohmic drop was then subtracted from the total overpotential. Rectangular wave form pulses were derived from an E. M. Test Pulser, Lawrence Berkeley Laboratory. The potentials were observed on a Tektronix Oscilloscope, and the potential trace was analyzed from the polaroid prints. The oscilloscope was operating at 0.01-1.0 msec/cm and 50-200 mV/cm. The ohmic drop was determined at four different currents for each cell, both in anodic and cathodic directions. The currents employed during the pulse measurements were higher than the currents employed during the micropolarization experiments, and it has been assumed that the current distribution remained unchanged. Typical oscilloscope traces of the potential during current interruptions both in the cathodic and the anodic directions, are presented in Fig. 1. Currents were in the order of 0.1-1.0 mA, and the calculated ohmic resistances were in the order of 100-300 ohms. The calculated resistance from the four measurements agreed within 10%.

The polarization experiments were conducted at different alkali metal chloride molalities in $AlCl_3$ (1*M*)-PC solution and 25°C.

Results

Micropolarization of the alkali metals in their chloride solutions in $AlCl_3$ (1M)-PC.—Micropolarizations of the alkali metals in different molalities of alkali metal chlorides in $AlCl_3$ (1*M*)-PC solution are presented in Fig. 2-6. The temperature was held constant at 25° ± 0.01°C. The overpotentials are *IR* free, and the ohmic drop was estimated from the current interrupter technique. At low overpotentials, linear behavior was observed for all the metals; deviation from linearity was observed at potentials above approximately 50 mV, where the nonlinear Tafel behavior became appreciable.

The exchange current densities were calculated from the slopes of the linear polarizations, assuming single electron charge transfer controlled mechanism according to the equation

$$i_a^o = \frac{1}{A}\frac{RT}{F}\frac{\partial i}{\partial \eta_{i=0}} \qquad [2]$$

and the results are presented in each figure (Fig. 2-6).

Enthalpy of activation at zero polarization.—Micropolarizations of the lithium electrode in different LiCl concentrations in $AlCl_3$ (1*M*)-PC were performed at three different temperatures: 25°, 30°, and 35°C. Fig-

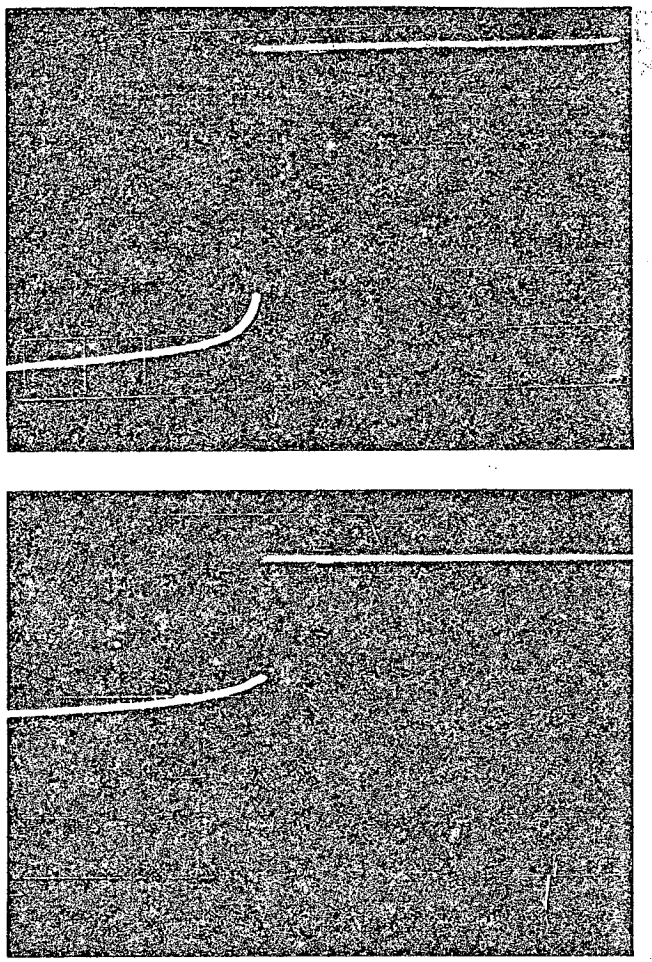

Fig. 1. *IR* drop determination in the six-compartment cell using a current interrupter technique. Rb/RbCl(0.10*M*) in $AlCl_3$(1.0*M*)-PC at 25°C. Top, cathodic current, I = 1.0 mA; bottom, anodic current, I = 0.5 mA. Vertical scale, 50 mV/cm; horizontal scale, 1 msec/cm.

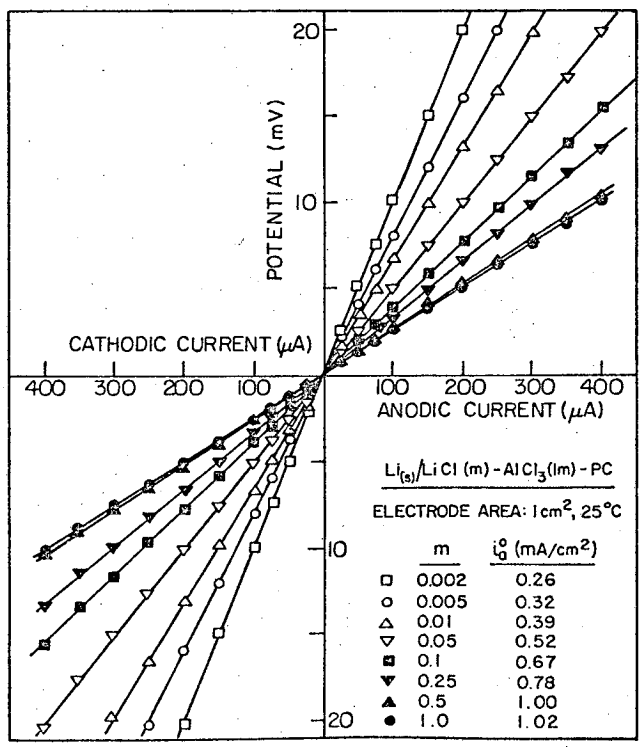

Fig. 2. Micropolarization of Li(s)/LiCl(*M*) in $AlCl_3$(1*M*)-PC solution.

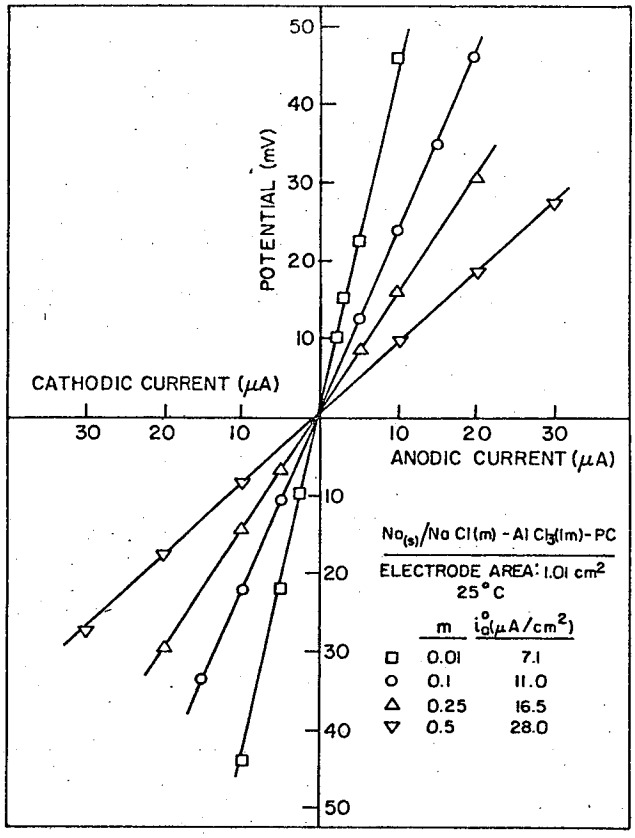

Fig. 3. Micropolarization of Na(s)/NaCl(M) in $AlCl_3$(1M)-PC solution.

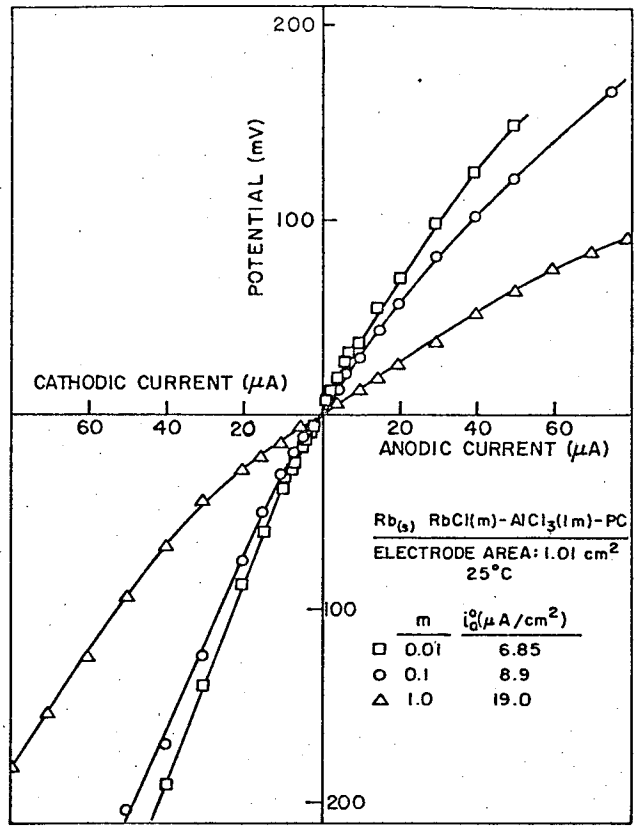

Fig. 5. Micropolarization of Rb(s)/RbCl(M) in $AlCl_3$(1M)-PC solution.

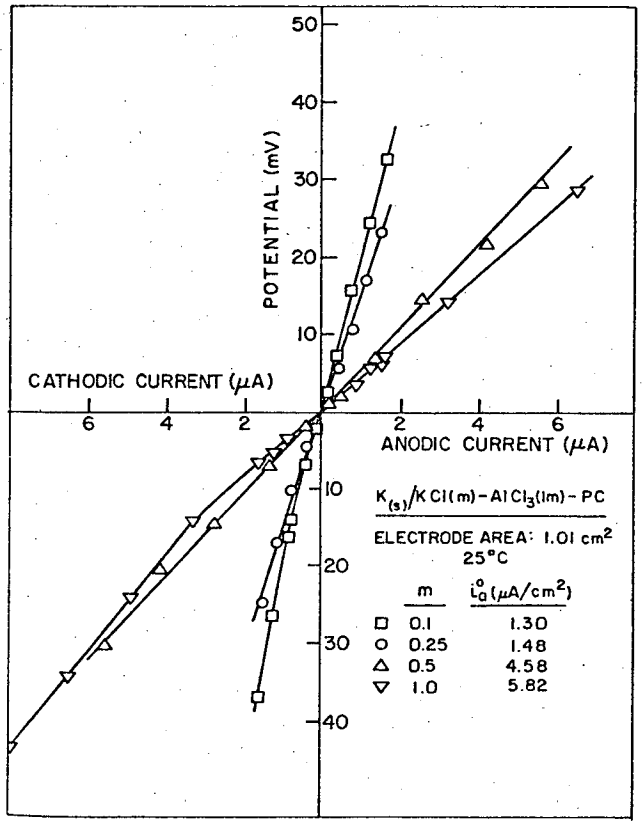

Fig. 4. Micropolarization of K(s)/KCl(M) in $AlCl_3$(1M)-PC solution.

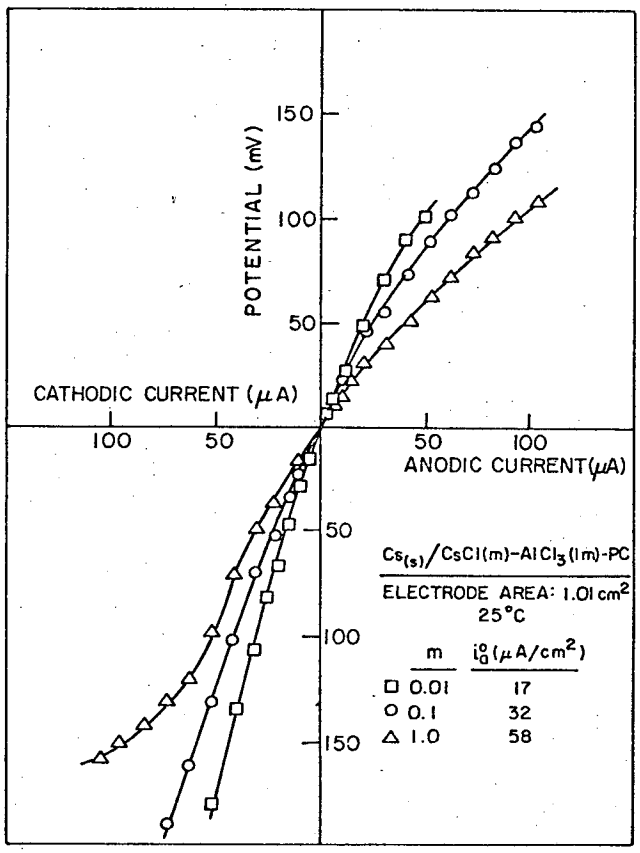

Fig. 6. Micropolarization of Cs(s)/CsCl(M) in $AlCl_3$(1M)-PC solution.

ure 7 presents the plot of the apparent exchange current densities, i_a°, *vs.* $1/T$ for the various LiCl molalities. The slopes of the lines are about equal, and the average enthalpy of activation at zero polarization was calculated as

$$\Delta H_o^* = -R\frac{\partial \ln i_a^\circ}{\partial (1/T)} = 8.6 \text{ kcal/mole} \qquad [3]$$

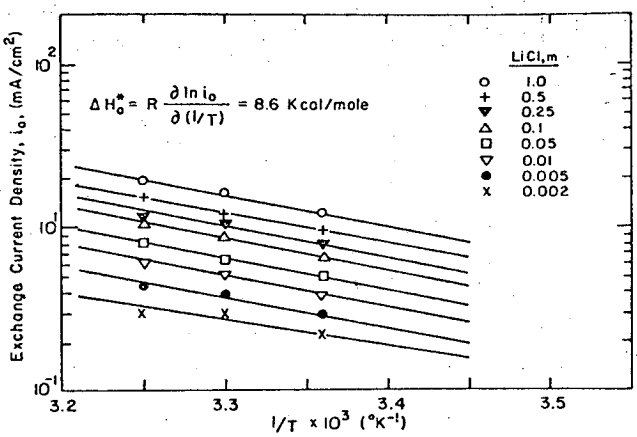

Fig. 7. Determination of the enthalpy of activation at zero polarization for Li/LiCl(M) in $AlCl_3$(1M)-PC solution.

The value of ΔH_o^* is within the order of magnitude expected for soft metals. A similar value of 7.1 kcal/mole was obtained for the sodium electrode in $NaClO_4$ solution in PC (1).

The micropolarization behavior of a cesium electrode in $CsAlCl_4$ (0.25M) solution in PC is presented in Fig. 8. The plot of i_a^o *vs.* $1/T$ is presented in Fig. 9, from which the enthalpy of activation at zero polarization is 10.4 kcal/mole. A somewhat lower exchange current density was obtained for the Cs electrode at 23.5°C. At this temperature cesium is solid, while the other temperatures employed are above the melting point of cesium, *i.e.*, 28.5°C.

Discussion

Micropolarizations of the alkali metals in alkali metal chloride solutions in $AlCl_3$ (1*M*)-PC were presented in Fig. 2-6. The apparent exchange current densities were calculated from the slopes at the point of zero current. A linear behavior can be observed for all

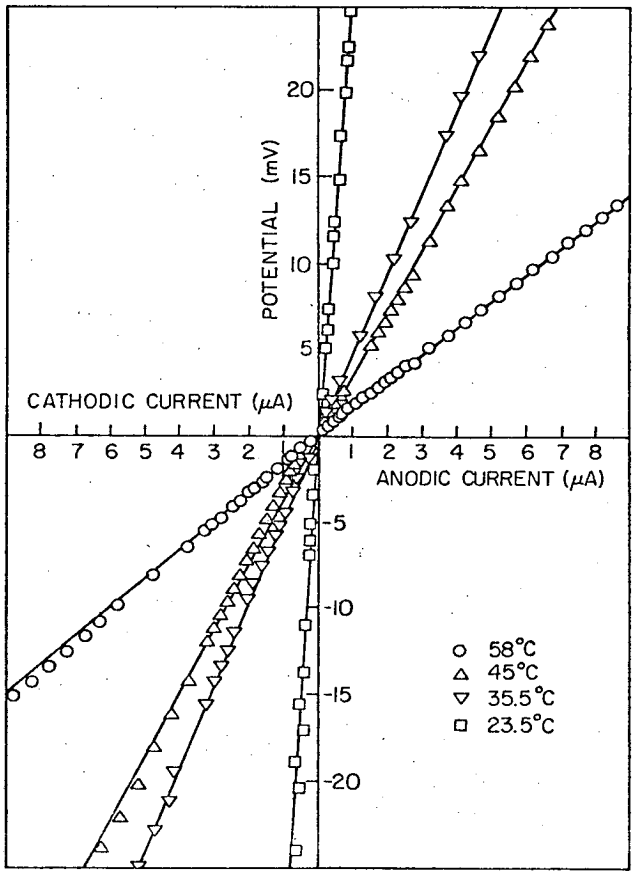

Fig. 8. Micropolarization of Cs(s)/$CsAlCl_4$(0.25M) in PC

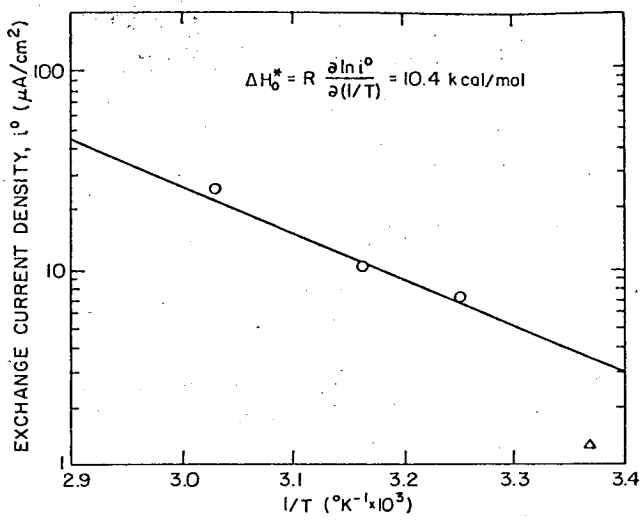

Fig. 9. Determination of the enthalpy of activation at zero polarization of Cs(s)/$CsAlCl_4$(0.25M), PC. ○, Liquid Cs; Δ, solid Cs.

the alkali metals over a wide range of alkali metal chloride concentrations. Using a low current and moderate stirring ensured the elimination of concentration overpotential. The apparent exchange current densities were not corrected for the nonuniform current densities across the surface of the electrodes. The influence of the nonuniformity of the current across the electrode is discussed in the Appendix, where it is shown that, despite relatively low conductivities, this correction is negligible for the present case, because of low exchange current densities.

The comparison of the magnitude of the exchange currents to corresponding values in the literature is restricted to the lithium system, because no information is available for the rest of the alkali metals. The exchange current density of Li in $LiAlCl_4$ (1*M*), according to the present results, is 1.02, 1.5, and 2.0 mA/cm² at 25°, 30°, and 35°C, respectively. These values are in general agreement with the exchange currents of 0.40, 1.05, 1.49, and 2.35 mA/cm² reported by Meibuhr (5) for $LiAlCl_4$ (1M) at 19°, 35°, 46°, and 55°C, respectively. A plot of the exchange current densities *vs.* $1/T$ is presented in Fig. 7, and the calculated enthalpy of activation at zero polarization, $\Delta H_o^* = 8.6$ kcal/mole, is in agreement with an enthalpy of 6.4 kcal/mole, reported by Meibuhr (5). Kinetic measurements of Li in $LiClO_4$ solutions in PC were performed by Meibuhr (4) and Scarr (6). The exchange current densities in $LiClO_4$ (1M) solution were 0.95, 1.8, 3.4, and 5.25 mA/cm² at 28°, 43°, 58°, and 67.5°C, respectively (4), and 1.78 mA/cm² at 23°C (6). The i^o values for $LiClO_4$ solution in PC are of the same order of magnitude as those obtained here for $LiAlCl_4$. Butler *et al.* (7) found that the current density changes significantly during the first few minutes after the preparation of a clean fresh Li surface. However, all earlier experiments, as well as the present ones, were performed on aged surfaces, which is a more practical condition. Preanodization of the surface was necessary to obtain reproducible results. It is not clear whether this procedure removes adsorbed impurities or breaks an insulating film on the electrode. Scarr (6) reports two levels of activities of Li electrode in $LiClO_4$ solution in PC, depending on the pretreatment of the surface, and the lower level of activity was associated with film formation.

The exchange current densities for the rest of the alkali metals are lower than those for Li. The wide differences in the exchange currents in the alkali metal series are discussed in detail elsewhere (1), where the medium effect and the influence of the individual ionic energetics on the electrode kinetics is discussed with regard to the behavior of the alkali metal amalgams.

The free energies of transfer of the alkali metal ions from water to $AlCl_3$-PC solution are: −0.6, −4.2, −4.7, −3.1, and −5.0 kcal/mole for Li^+, Na^+, K^+, Rb^+, and Cs^+, respectively (1). A large negative free energy of transfer means that the ion is on a low energy level, strongly solvated, and as a result, the exchange current density is low. The low exchange current densities of some of the alkali metals might also be the result of their reactivity toward impurities, water traces, and possibly the solvent itself. This is especially true for potassium, which showed reactivity toward PC solutions which had not been treated with molecular sieves.

The exchange current density of a Na electrode in NaCl(0.5*M*) solution in $AlCl_3$ (1*M*)-PC is 28 $\mu A/cm^2$ at 25°C, which can be compared qualitatively to a value of 12 $\mu A/cm^2$ for a Na electrode in $NaClO_4$(0.5M) solution in PC at 19°C (11).

The reported exchange current densities are subjected to the influence of the films formed due to the inherent reactivity of the alkali metals with PC. Film formation was observed on Li electrodes in PC (6, 23).

The transfer coefficients of the electrochemical reaction at the alkali metal electrode interface can be calculated from the dependence of the exchange current density on the concentration of the reduced ion (19, 20)

$$1 - \alpha_c = \frac{\partial \log i_a^o}{\partial \log m_{M^+}} \qquad [4]$$

where α_c is the cathodic transfer coefficient. Figure 10 presents the plot of log i_a^o *vs.* log m_{MCl} for all the alkali metals, as well as the calculated α_c. The cathodic transfer coefficient for Li is $\alpha_c = 0.75$, in agreement with $\alpha_c = 0.8$ reported for $LiAlCl_4$ in PC, and $\alpha_c = 0.62$-0.72 for $LiClO_4$ in PC (4-6). The lithium system was further investigated at three different temperatures, 25°, 30°, and 35°C. The plots of log i_a^o *vs.* log m_{LiCl} at the three temperatures are presented in Fig. 11, and the parallel lines show that the transfer coefficient does not change over this temperature range. An average $\alpha_c = 0.75 \pm 0.05$ was calculated for the three temperatures.

The behavior of the alkali metals in the Tafel region should be investigated in the future. Cyclic polarizations were obtained for K, Rb, and Cs and are covering the Tafel region (1). Although the polarizations include the ohmic drop between the working and the reference electrode, Tafel behavior can nevertheless be observed qualitatively in some of these figures. It is believed that the exchange currents in this region are higher than the values obtained in the micropolarization experiments because of continuous renewal of the active surface and the breakage of possible film formation at high deposition or dissolution rates.

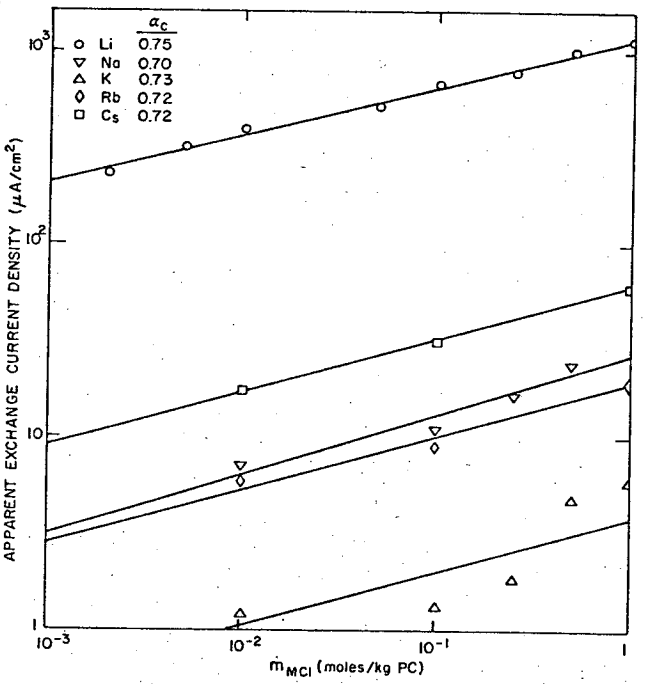

Fig. 10. Determination of the cathodic transfer coefficients of the alkali metals in $AlCl_3$(1*M*)-PC.

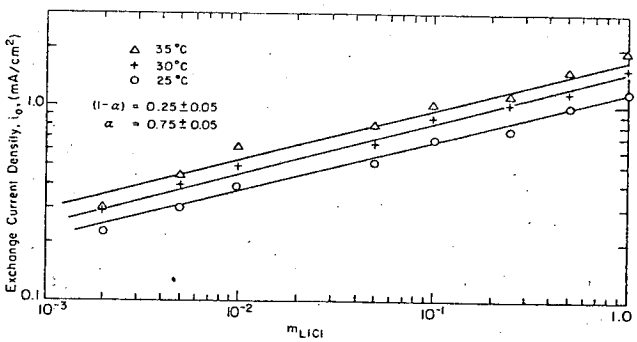

Fig. 11. Determination of the cathodic transfer coefficients of Li in $AlCl_3$(1*M*)-PC at 25°, 30°, and 35°C.

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1975 JOURNAL. All discussions for the June 1975 Discussion Section should be submitted by Feb. 1, 1975.

APPENDIX

Nonuniform Current Distribution and Ohmic Drop Effects in Micropolarization Measurements

Under nonuniform current density conditions, the exchange current, i^o, determined from the linear polarization, depends on the location of the reference electrode, because the measured overpotential is related to the local current density which differs from the average current density. The correction can be obtained by solving the secondary current distribution subjected to a boundary condition of linear polarization. The present analysis follows the treatment of Tiedemann, Newman, and Bennion (21) concerning the error in measurements of electrode kinetics caused by nonuniform ohmic potential drop to a disk electrode.

The correction for the apparent exchange current $i^o/i^o_{apparent}$ was solved for the general arbitrary location of the reference electrode (21), and is plotted against J

$$J = (\alpha_a + \alpha_c)\frac{\mathbf{F} r_o i^o}{RT\kappa_\infty}$$

J represents, in a way, the throwing power of the system.

The exchange current densities reported in the present work are the apparent ones; however, the corrections are negligible. Considering the extreme conditions, $r = 0.5$ cm, $\kappa_\infty = 5 \times 10^{-3}$ ohm^{-1}-cm^{-1}, $i^o = 1.0$ mA/cm^2, and assuming $(\alpha_c + \alpha_a) = 1$, we can estimate the largest possible J for the present systems to be

$$J = 4$$

Since the reference electrodes were located far away from the disk electrode, the correction, according to curve B in Fig. 1 (21) is about $i^o/i^o_{apparent} = 1.1$, which

is negligible, especially since the errors in the exchange current values are probably more than 10%. It should be mentioned here that the extreme conditions given above were realistic only for the lithium system. For the rest of the alkali metals the exchange current densities are ten times lower, and the conductivities are somewhat higher, both resulting in lower J, and the correction is probably in the order of 1%.

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Mass Transfer of Minor Components in a Propagating Crack

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ABSTRACT

The mass transfer of a dilute species in a liquid in a propagating crack is treated. The analysis includes the effect of convective flow of the liquid. The results of the calculations show that the crack tip is devoid of the minor species, and that the mass flux of this component is also negligible in this region. Therefore, minor components could not behave as "critical" species in such systems. Calculation of the flux distribution allowed the determination of the potential distribution in the crack.

The failure of structural materials such as metals and their alloys by stress corrosion cracking is a complex phenomenon which involves the interplay of metallurgical, mechanical, and enviromental influences. For an alloy of a particular metallurgical condition in a constant environment, the crack propagation may be investigated as a function of stress intensity,[1] a mechanical variable. It is generally found for titanium and aluminum alloys (1-3) that the rate of crack extension is dependent on the stress intensity at low stress levels but becomes independent of the stress intensity at higher levels. Several workers (4-6) have suggested that the process limiting the crack growth rate at high stress intensities is related to mass transfer of components in the environment. "Cavitation" caused by limitations on the fluid flow in a propagating crack could also limit the cracking rate, as discussed recently (7).

The alloy titanium-8% aluminum-1% molybdenum-1% vanadium has been found to be susceptible to stress corrosion cracking in molten LiCl-KCl eutectic (8). A plateau velocity of 1 cm/sec was observed at high stress intensities, and the crack extension rates were a function of stress intensity at lower stress intensities. The presence of the plateau velocity could not be explained by cavitation (7), so the possible role of mass transfer has been investigated. Possible species which could limit the rate of crack extension in the molten salt environment are Li^+, K^+, or some impurity such as H_2O (or OH^-). The first two are ruled out by the dependence of the cracking rate on electrical potential (8, 9). Water was present in the commercial eutectic material at about 1 ppm (reported as OH^-), and the SCC tests were carried out under potential conditions

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[1] The stress intensity is related to the stress, flaw size, and specimen geometry for materials which obey the laws of linear elastic fracture mechanics (1, 2).

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